AGD Surface Modification on Nanofibers to Improve Dispersion and Interfacial Bonding (FA5209-06-P-0187)

Report

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Report Documentation Page		*Form Approved* *OMB No. 0704-0188*

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1. REPORT DATE **26 MAY 2007**	2. REPORT TYPE **FInal**	3. DATES COVERED **08-05-2006 to 22-05-2007**
4. TITLE AND SUBTITLE **AGD Surface Modification on Nanofibers to Improve Dispersion and Interfacial Bonding**		5a. CONTRACT NUMBER **FA520906P0187**
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Byung-Sun Kim**		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Korea Institute of Machinery & Materials,66 SangnamDong ,Changwon 641-010,Korea (South),KR,641-010**		8. PERFORMING ORGANIZATION REPORT NUMBER **; AOARD-054100**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AOARD, UNIT 45002, APO, AP, 96337-5002**		10. SPONSOR/MONITOR'S ACRONYM(S) **AOARD-054100**
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) **AOARD-054100**
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES		

14. ABSTRACT

Vapor grown carbon fibers (VGCF) were plasma treated before added to PP (propylene) and epoxy, respectively, in an attempt to improve the fiber?s dispersion and interfacial bonding with the matrix. To disperse VGCF within PP, Hexamethyl-disiloxane was used to coat the fibers and to disperse VGCF within epoxy, the VGCF?s were surface grafted with hydrophilic property that is most compatible with epoxy. For the case with PP, the dispersion of nanofibers was carried out by solution blending, mechanical mixing, and sonication. Levels of 4% ? 31% volume content of VGCFs were mixed with polypropylene (PP) powder, and then were melt-mixed using a twin-screw extruder in order to align the fibers. For the further alignment of fibers, extruded rods obtained by twin screw extruder were stacked in the mold cavity for the compression molding. In the case of 31% volume content, the tensile modulus and strength were improved by 100% and 40%, respectively, and the flexural modulus and strength were increased by 120% and 25%, respectively. The shear modulus showed 65% increase, but the strength dropped sharply by 40%. In the transverse direction, the tensile, flexural, and shear strength decreased as more fibers were added. The matrix modification by maleic anhydride (MAPP) increased the tensile and flexural properties of VGCF/PP by 20% - 30% in the longitudinal direction, and 40% - 250% increase in the transverse direction. The fiber surface treatment by plasma improved tensile and flexural properties of untreated VGCF/PP (18 % vol) composites by 10% - 30% in the longitudinal direction, but strength in the transverse direction decreased by 30% - 40%. For the case with epoxy, the dispersion of nanofibers was also carried out by solution blending, mechanical mixing, and sonication. Levels of 1 ? 7wt% content of VGCFs were mixed within epoxy. The Atmospheric Plasma Treated (APT) VGCF?s had much higher adhesive strength with epoxy matrix than raw VGCF?s. The modulus of raw VGCF and AFT VGCF/epoxy had the similar values. The VGCF?s were well dispersed with ethanol addition with ultrasonic and solution blending method in 30 minutes. The uniform dispersion of VGCF seen by scanning electron microscopy (SEM) showed an excellent dispersion of VGCF in epoxy by solution blending and ultrasonic method, respectively. The mechanical properties of VGCF/epoxy by using ultrasonic method were higher than that of solution blending method.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE	**Same as Report (SAR)**	**19**	
unclassified	**unclassified**	**unclassified**			

Abstract

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To disperse VGCF within PP, Hexamethyl-disiloxane was used to coat the fibers and to disperse VGCF within epoxy, the VGCF's were surface grafted with hydrophilic property that is most compatible with epoxy.

For the case with PP, the dispersion of nanofibers was carried out by solution blending, mechanical mixing, and sonication. Levels of 4% − 31% volume content of VGCFs were mixed with polypropylene (PP) powder, and then were melt-mixed using a twin-screw extruder in order to align the fibers. For the further alignment of fibers, extruded rods obtained by twin screw extruder were stacked in the mold cavity for the compression molding. In the case of 31% volume content, the tensile modulus and strength were improved by 100% and 40%, respectively, and the flexural modulus and strength were increased by 120% and 25%, respectively. The shear modulus showed 65% increase, but the strength dropped sharply by 40%. In the transverse direction, the tensile, flexural, and shear strength decreased as more fibers were added. The matrix modification by maleic anhydride (MAPP) increased the tensile and flexural properties of VGCF/PP by 20% - 30% in the longitudinal direction, and 40% - 250% increase in the transverse direction. The fiber surface treatment by plasma improved tensile and flexural properties of untreated VGCF/PP (18 % vol) composites by 10% - 30% in the longitudinal direction, but strength in the transverse direction decreased by 30% - 40%.

For the case with epoxy, the dispersion of nanofibers was also carried out by solution blending, mechanical mixing, and sonication. Levels of 1 − 7wt% content of

VGCFs were mixed within epoxy. The Atmospheric Plasma Treated (APT) VGCF's had much higher adhesive strength with epoxy matrix than raw VGCF's. The modulus of raw VGCF and AFT VGCF/epoxy had the similar values. The VGCF's were well dispersed with ethanol addition with ultrasonic and solution blending method in 30 minutes. The uniform dispersion of VGCF seen by scanning electron microscopy (SEM) showed an excellent dispersion of VGCF in epoxy by solution blending and ultrasonic method, respectively. The mechanical properties of VGCF/epoxy by using ultrasonic method were higher than that of solution blending method.

Introduction

There are increasing interests of vapor grown carbon nanofibers (VGCFs) for the reinforcements of polymeric materials due to their excellent mechanical, electrical, and thermal properties. In the processing of nanocomposites, their bulk properties are not only functions of the state of fiber dispersion and orientation, but also the interface between the fiber and matrix. VGCFs have been used to reinforce a variety of thermoplastic and thermosetting polymers. Compared with the micro-sized carbon fibers, nanofibers are favorable in the type of thermoplastic compounding owing to the less fiber breakage and the higher aspect ratio. Processing of thermoplastics provides additional advantages of recycling, cost-effectiveness, and environmental benefits due to free of solvents [1]. Among several processing methods for thermoplastic materials, melt-mixing of nanofibers into composites by extrusion process has captured considerable interest. In this process, an extruder die consists of funnel-shaped portion and annular portion, which generates converging flow and shear flow patterns in producing fiber alignment. The process variables of extrusion include the length, the

diameter, and the temperature of the nozzle exit. The longer nozzle of an extruder die gave higher tensile modulus and strength due to the better fiber alignment in the extended length [2]. Most of previous works on nanocomposites utilizing the melt-mixing process studied fiber weight fraction up to 15%. While the observed tensile modulus and strength improved significantly in the case of 11 %vol [2], the further enhancement is likely if more fibers are added. Among other post-processing methods, the fiber spinning by a spinneret demonstrated the potential of structural usage of nanocomposites [3, 4]. With only 5% fiber volume content of VGCFs/PP, the tensile strength and modulus increased by 16% and 54%, respectively, and the compressive strength was doubled to that of neat PP material [3]. Choi et al reported that only a small amount (1-3 wt%) of VGCF highly increased the modulus and stresses of epoxy matrix [5]. In addition to these facts, the bonding at the VGCF/epoxy interface is extremely important for the improvement of mechanical properties with increasing amount of VGCF. Surface modification of VGCF has been studies for many years, and several methods were used plasma treatment with some materials coating such as oxygen, water, carbon dioxide, ammonia, formic acid or monomer. Thereby, oxygen and nitrogen containing groups may be introduced onto the surface of VGCF [6-9]. The purpose of this study is to provide techniques of dispersion and alignment of high volume contents of nanofibers, and to examine the effect of fiber contents on the mechanical properties of VGCF/PP and VGCF/Ep composites, respectively.

Experiments

AGD plasma polymerization

Atmospheric glow discharge (AGD) was developed with industrial plasma sources by using high voltage radio frequency (RF) excitation at KHz frequency ranges.   It is possible to produce a steady-state uniform glow discharge at atmospheric pressure with various gases, thus eliminating the requirement of a vacuum system to expose the materials to plasma.   The RF frequency should be in the right range: if it is too low, the discharge will not initiate and if it is too high, the plasma will form filamentary discharge between electrode plates or will be transformed to arc discharge.   Therefore, only in the limited range of frequency band can the AGD be produced.   The advantage of AGD is to modify or coat the materials with good uniformity and to produce modified or coated materials continuously.

The AGD plasma polymerization can be used to modify the surface properties of nanofibers or nanopowders to improve the compatibility among these nanoconstituents themselves as well as between the nanoconstituents and the polymeric matrix materials. The AGD surface modification process can allow the nanoconstituents to disperse quite evenly within the matrix with a strong interfacial bonding between the nanoconstituents and the matrix material.   This process can put some functional groups on the surface of materials as acrylic, epoxy, amine, hydroxyl, etc.   This process can be achieved continuously in a single step.

Contact angles of AGD polymer of various monomer liquids is measured by goniometer and their surface energy is calculated to find the most suitable monomer liquid.   Helium is used as a carrier gas and the most suitable monomer liquid is used to modify the surface property by plasma polymerization.   The reactor is operated at a

room temperature while the surface is modified at atmospheric pressure.
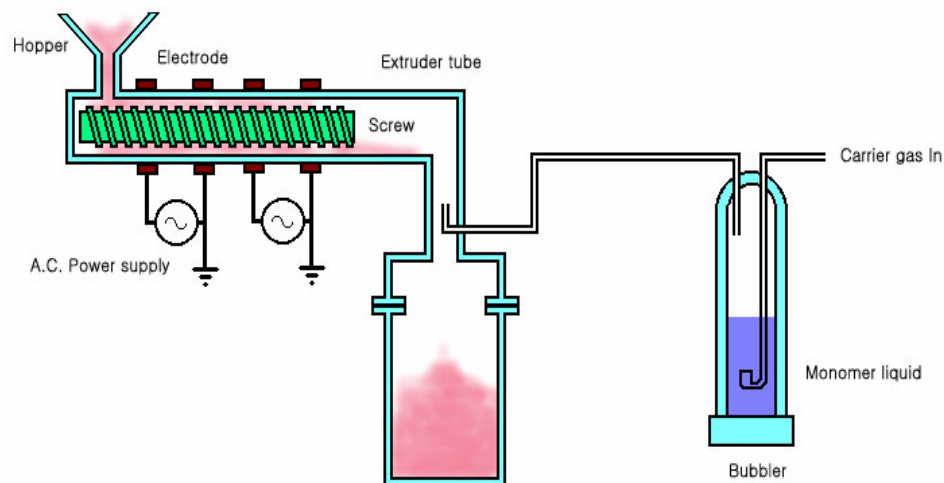
Schematic drawing of AGD polymerization process

Materials

Commercially available VGCF (VGCF® -H), manufactured by Showa Denko KK, were used in this study. VGCF®-H is the VGCF specifically designed to enhance the electrical and thermal properties of high performance materials. VGCF® -H is specially processed to improve dispersion and homogeneity.

Typical Properties of VGCF (Showa Denko, Japan)

Fiber diameter	nm	150
Fiber length	μm	10-20
Real density	g/cm^3	2.0
Bulk density	g/cm^3	0.04
Specific surface area	m^2/g	13
Aspect ratio	Fiber length/diameter	60
Electrical resistivity	Ωcm	1x10^4
Conductivity	powder resistivity: Ωcm	0.013
Dispersion	Good	

Raw VGCF and APT VGCF were applied for Epoxy YD 128 and processed with the anhydride curing agent methyltetrahydrophthalic anhydride, MTHPA, Kukdo®, KBH-

1089 (Kukdo Chemical). The mixing ratio of epoxy and curing agent was 100/90wt [16].

Dispersion by mechanical mixing
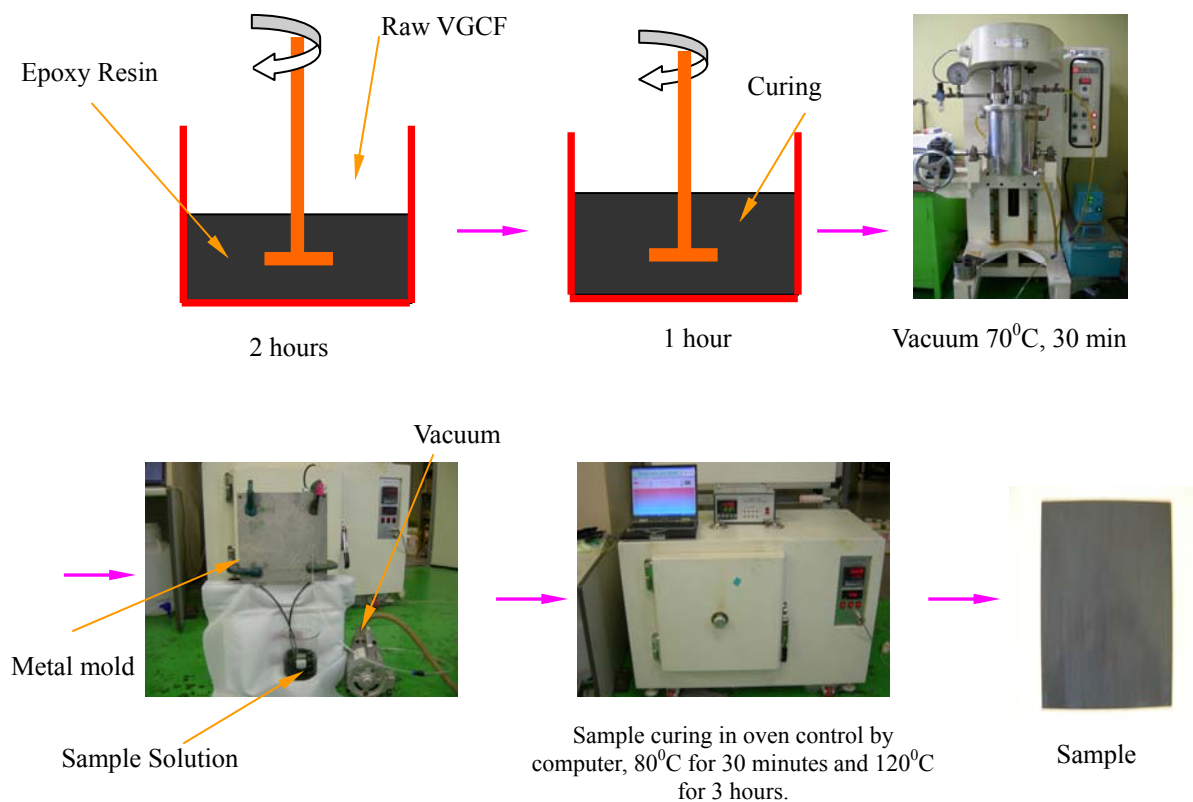
Process 1: Mechanical mixing method

Dispersion by solution blending

The ethanol extracted by vacuum at 85^0C for 2 hrs

Rest of the step similar to Mechanical mixing.
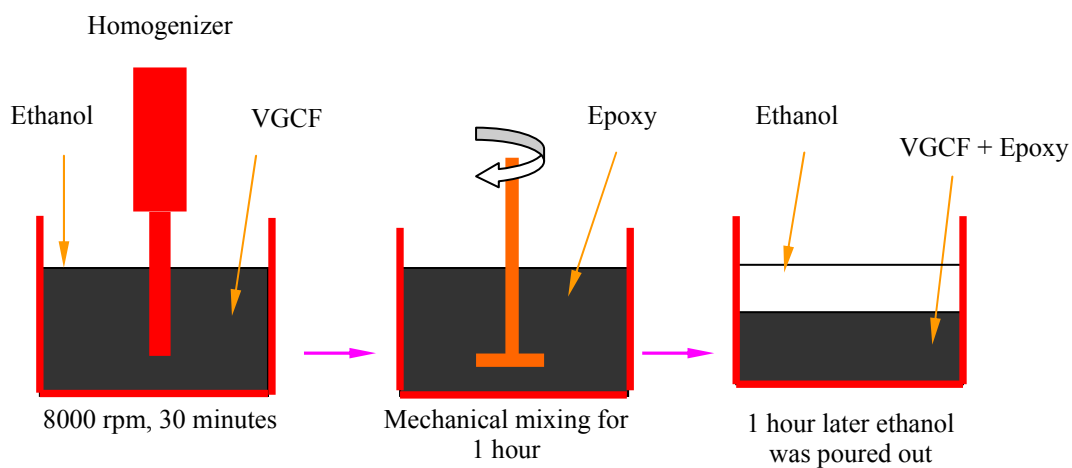
Process 2: Solution Blending Method

Dispersion by ultrasonic

Fig. 1: Ultrasonic

VGCF/PP composite

The carbon nanofibers VGCF™, having an aspect ratio 10-500 were supplied by SDK, Japan. Polypropylene (PP) was obtained from KOLON, Korea in a powder form of particle size in 0.5 – 1 mm range. In order to disperse carbon nanofibers, they were mixed
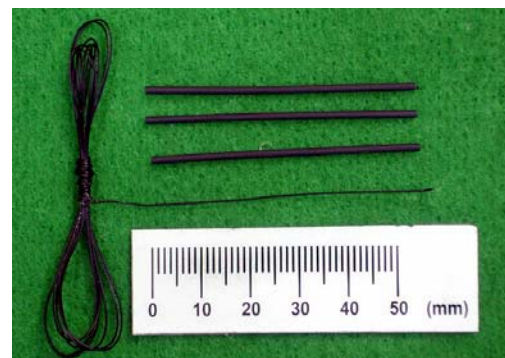
Fig. 1 Extruded rods and a fiber

with ethyl alcohol in 1:20 ratio, and then stirred for 1 h mechanically. The mixture of fiber/alcohol was sonicated 10 times for 1 min each, and then specified amount of PP powder was added to the mixture. After mechanical agitation of the mixture for 1 h again, it was vacuum dried at 80 ^{o}C for over 48 h. In order to examine the effect of matrix modification, 3% weight of maleic anhydride was added to PP (MAPP). The effect of fiber surface modification for the uniform dispersion of fibers and for the improvement of fiber/matrix interfacial strength was also investigated by treating fiber surface with plasma using atmospheric glow discharge.
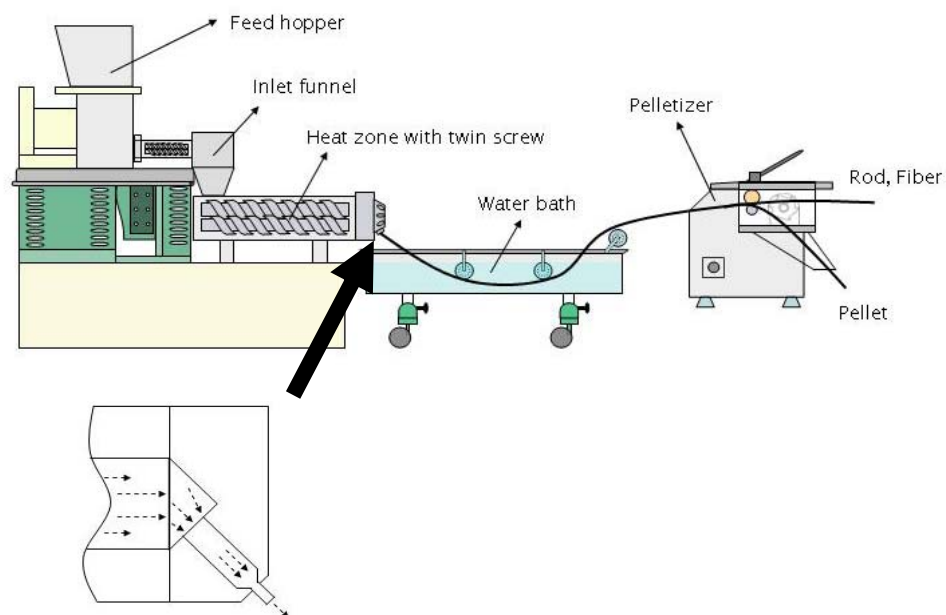
• Funnel-shaped portion and annular portion

• Converging flow and shear flow patterns

fiber alignment

Melt-mixing was conducted on a twin-screw extruder. With this opening of 0.5 mm, composites rods of continuous and consistent diameter have been fabricated. The extruded composites were quenched in a bath of room temperature water. As a control material, PP rods were also prepared by extrusion process. The volume contents of VGCFs were varied from 4% to 31%. The diameter of a rod was in the range 1 – 2mm.

Test samples were prepared by cutting and stacking the rods into a 250 x 80 mm^2 mold, which was subjected to compression by press. The sample thickness was in the range of 2.8 – 3.0 mm. Tensile, flexural, and in-plane shear test specimens were conformed to ASTM D638 Type IV, ASTM D790M, and ASTM D5379, respectively. Five samples were tested for each case.

VGCF/Ep composite

To fabricate the VGCF/epoxy by mechanical mixing method, 0 – 7 wt% raw VGCF were mixed in epoxy for 2 hours, respectively. Curing agent was blended with the mixture with mechanical stirring for 1 hour. The air bubbles are removed by vacuum at 70^{0}C for 30 minutes. The epoxy matrix was injected into metal plate mold with vacuum to produce a plate specimen. The specimens were cured at 80^{0}C for 30 minutes, and then for 3 hours at 120^{0}C (Process 1).

To make the raw VGCF/epoxy (up to 3 wt%) by solution blending method, the raw VGCF were dispersed in ethanol for 30 minutes by using a Specification® homogenizer (Global Lab) at 10.000 rpm. The solution contained more than 100 ml of ethanol to 1g of VGCF. The epoxy was then added and mixed under continuous mechanical mixing for an additional hour. 1 hour later, the mixture was divided into two layers (the upper layer was ethanol). The ethanol was poured out and the remaining portion was removed

by the vacuum at 85ºC for 2 hours. All following steps were similar to those of mechanical mixing method (Process 2).

To make the VGCF/epoxy nanocomposites (up to 3 wt%) by ultrasonic, the VGCF were sonicated in ethanol for 30 minutes by using a Sonic Mater® sonicator (The Sonic Tech, Co.Ltd). All following steps were similar to those of solution blending method. The raw VGCF and APT VGCF were used in this processing, respectively. Tensile test specimen was fabricated accordance with ASTM D638.

Results and Discussion

Fig. 2 shows SEM micrographs of fractured surfaces of a VGCF/PP composite rod (30 %vol) in the perpendicular to the extrusion direction. Entanglement of nanofibers is hardly seen, indicating fairly uniform fiber distribution. Although shear flow occurred in entering annular portion of the extruder die, fiber arrangement was not fully aligned as shown in Fig. 2 (b). This is due to the fact that fibers of smaller aspect ratio tend to be positioned in three-dimensional arrangement. However, section in the longitudinal direction shows relatively better alignment as shown in Fig. 2 (c).

(a) 65X   (b) 5000X   (c) 5000X
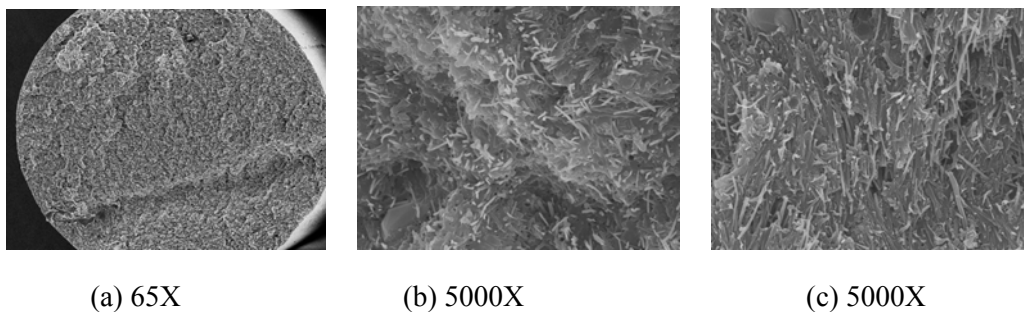
Fig. 2 SEM micrographs of VGCF 30 %vol /PP composites: (a), (b) cross-section; (c) longitudinal section.

Fig. 3 gives the tensile modulus and strength of VGCF/PP composites as a function of fiber volume content. Property normalization was based upon the PP material without fiber addition. In order to identify the fiber alignment, the longitudinal loading direction is defined as the direction of extrusion. The strength in the longitudinal direction is higher than that in the transverse direction. This clearly demonstrates that fibers are aligned in the longitudinal direction by extrusion process. The transverse tensile strength decreases with fiber contents while Young's modulus increases. In the transverse direction VGCFs act as defects rather than reinforcements. By addition of MA, tensile modulus and strength increased greatly, except for the case of modulus of 31 %vol. Plasma treatment was also effective for the improvement of mechanical property except for the transverse tensile strength.

(a)   (b)
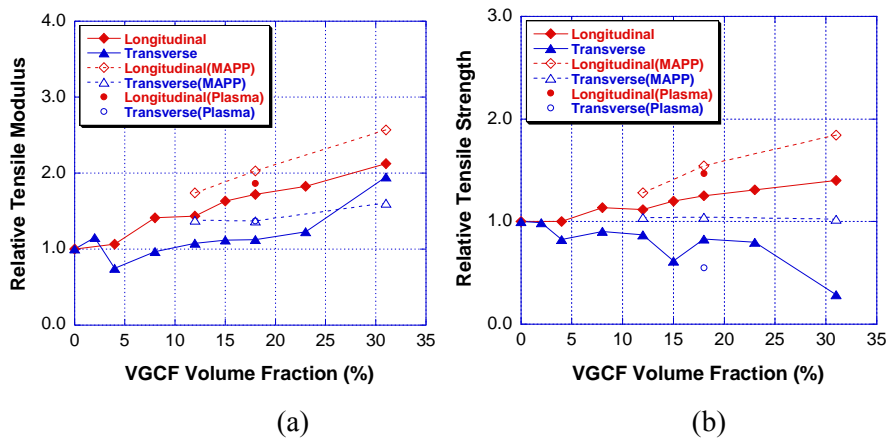
Fig. 3 Relative longitudinal and transverse tensile properties of VGCF/PP composites as a function of fiber volume content (4, 8, 12, 15, 18, 23, 31%): (a) Young's modulus; (b) strength.

Fig. 4 shows the variation of flexural properties with respect to the VGCF content. For 31 % volume content, longitudinal flexural modulus and strength were the highest. At low fiber contents, flexural properties are smaller than the neat PP. This may be due to the poor adhesion between fibers and matrix. The reduction of transverse strength with the increase of fiber contents is due to the higher population of stress concentrations. Similar to the tensile property, addition of MA was effective in the notable improvement of flexural property. In the longitudinal direction, modulus and strength increased by 30% and 20%, respectively. The improvement of flexural property is even great in the transverse direction: 40% and 140% increase in modulus and strength for 31 %vol. The plasma treatment increased the flexural property, except for the transverse strength.

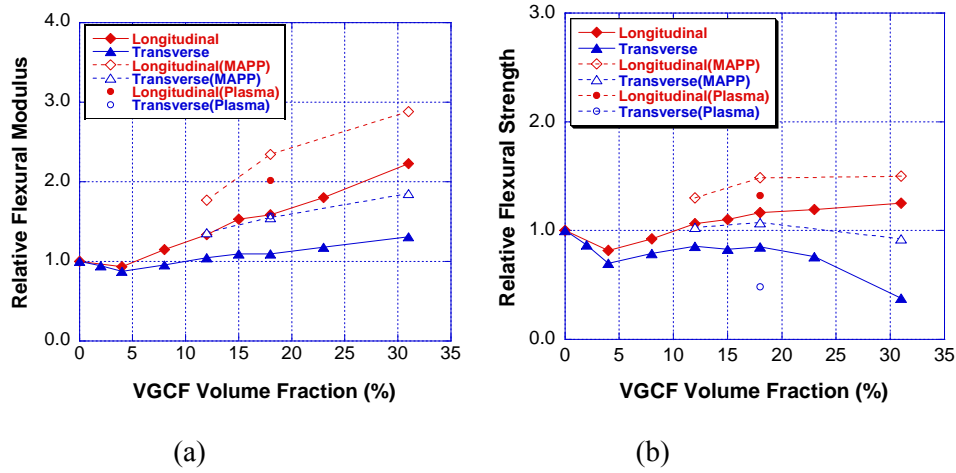(a)   (b)

Fig. 4 Relative longitudinal and transverse flexural properties of VGCF/PP composites as a function of fiber volume content (4, 8, 12, 15, 18, 23, 31%): (a) modulus; (b) strength.

Fig. 5 shows the relative shear modulus and strength of VGCF/PP composites as a function of fiber volume contents. Properties vary with some fluctuations, but the case of 31%vol shows the largest change. The increased shear modulus is due to the 3D orientation of fibers in this highly packed condition. The lower shear strength at 31 %vol is associated with the increase of stress concentration. The improvement of shear modulus of MAPP is tremendous for the cases of 12 % and 18% vol. Higher than VGCF 18 %vol, MAPP has little effect on the improvement of both the shear modulus and strength.
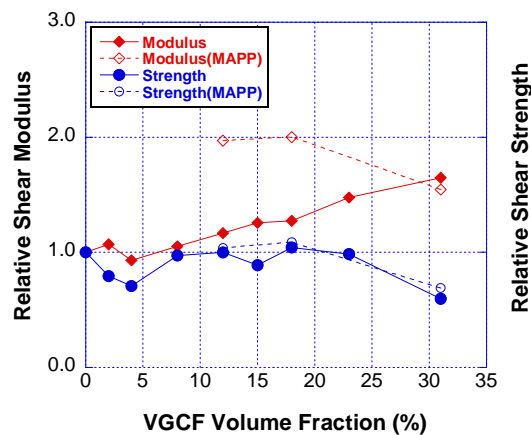
Fig. 5 Relative in-plane shear properties.

Effect of VGCF contents in epoxy matrix
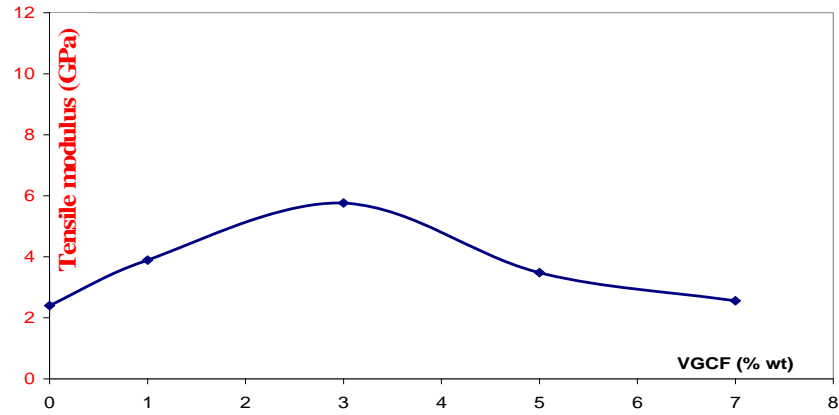
Fig. 6: The relation between the modulus and VGCF contents

VGCF/epoxy nanocomposites containing 3 wt% raw VGCF shows the maximum tensile modulus value (Fig. 6). The tensile strength of 3 wt% raw VGCF contents shows the highest value (Fig. 7).
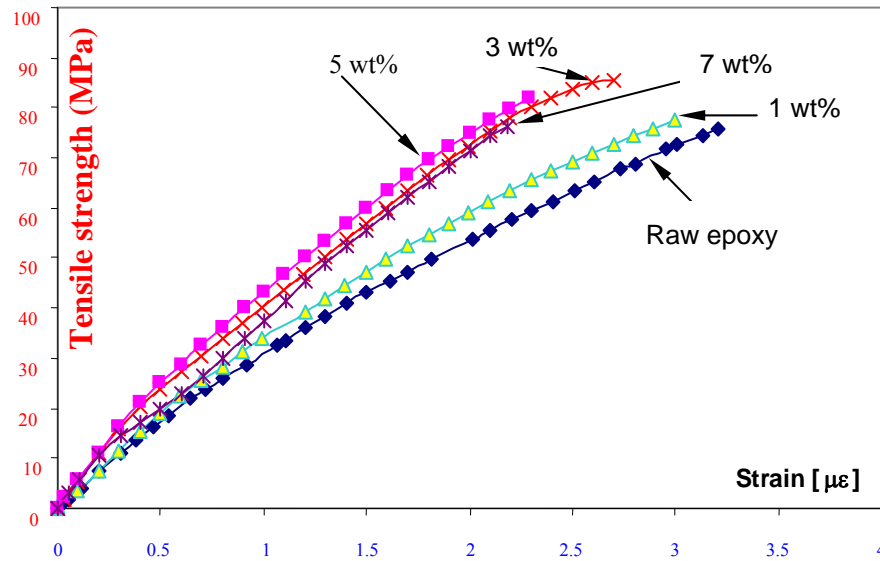

Fig. 7: The relation between the stress and VGCF contents

Modulus of raw and APT VGCF/epoxy

The tensile modulus of VGCF/epoxy nanocomposites by using ultrasonic method was higher than that of using solution blending method with the same VGCF contents (Epoxy YD 128) (Fig. 8). The tensile modulus of APT VGCF and raw VGCF/epoxy were the same as using ultrasonic method (Fig. 9 and 10).
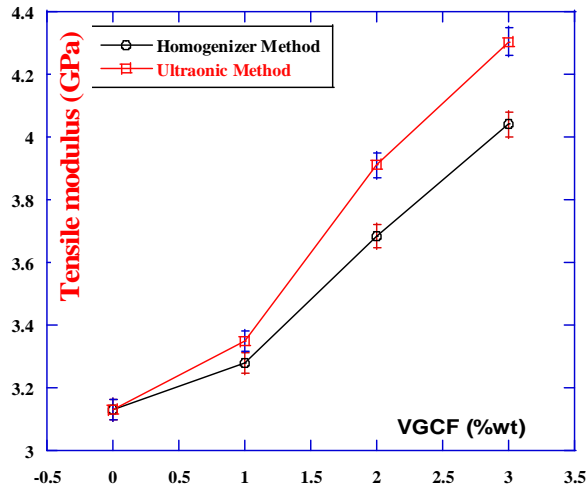
Fig. 8: The tensile modulus of raw VGCF/epoxy matrix with ultrasonic and homogenizer method
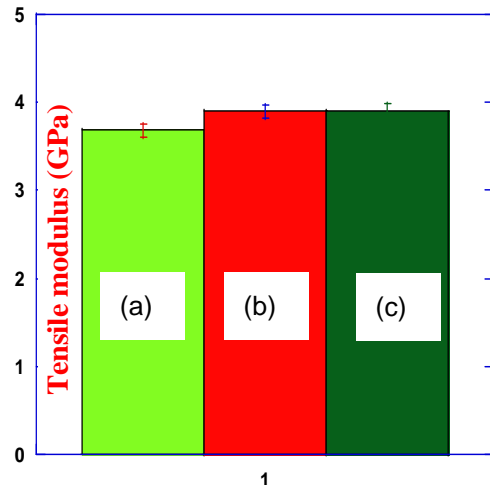
Fig. 9: (a) 2 wt% VGCF contents, solution blending method. (b), (c) 2 wt% APT VGCF and raw VGCF, ultrasonic method, respectively.
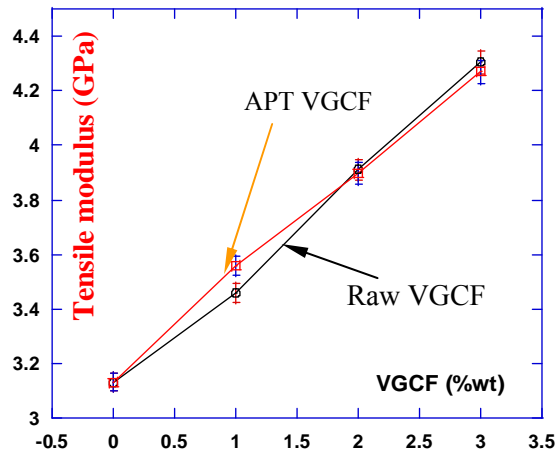

Fig. 10: The tensile modulus of raw VGCF and APT VGCF

Tensile strength of raw and APT VGCF/epoxy

The tensile strengths were increased with VGCF contents but the strains were decreased. The tensile strength of APT VGCF/epoxy matrix was higher than that of raw VGCF with the same ultrasonic method.

The surface of VGCF was plasma treated to improve the interfacial bonding strength between VGCF and epoxy matrix. Thereby, the tensile strength of APT VGCF/epoxy matrix was higher than that of raw VGCF with the same amount of VGCF contents (Fig. 11).
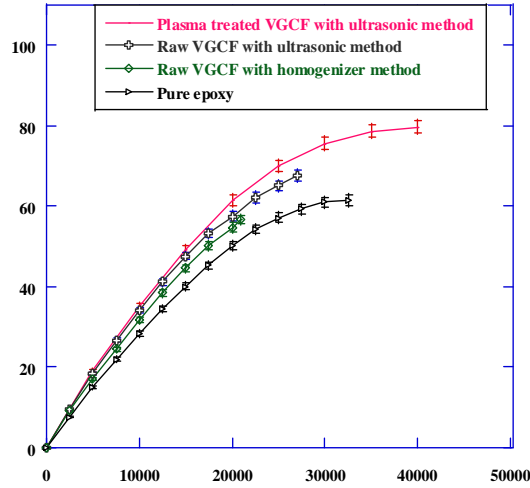

Fig. 11:   The tensile strength of raw VGCF and APT VGCF (2 wt%)/epoxy with ultrasonic and solution blending method.

Effect of using APT VGCF

The SEM photographs of the fracture surfaces showed the pulled-out VGCF's all over the fracture surfaces (Fig. 12). This implies that the adhesion between the raw VGCF and epoxy matrix was poor.

Stronger adhesion at the VGCF/epoxy interface was obtained with the plasma treated VGCF, which created higher surface energy on the VGCF surfaces due to very high interfacial bonding strength. Thereby, the tensile strength of PTA VGCF/epoxy matrix was quite high. From Fig. 13, only a few fibers are pulled out indicating the improved adhesion at VGCF/epoxy interface.
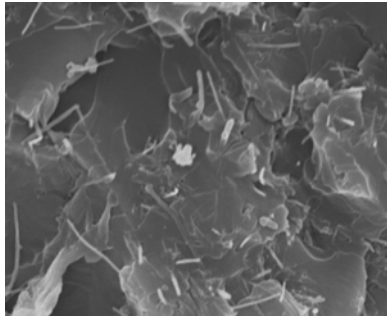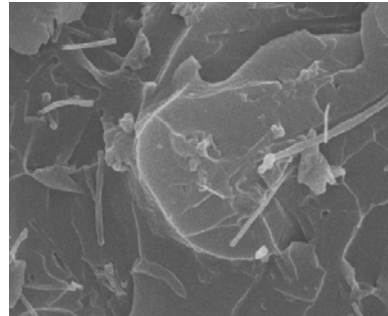

Fig. 12: Raw VGCF (2 wt %)

Fig. 13: APT VGCF (2 wt %)

Dispersion

The SEM showed not good dispersion of raw VGCF in epoxy matrix with mechanical mixing method (Fig. 14)
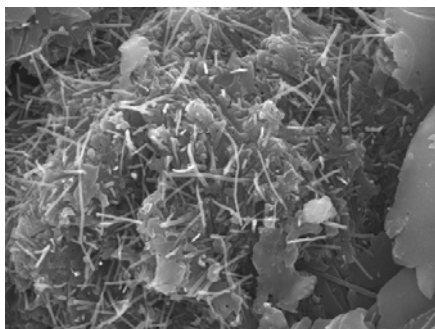

Fig. 14: raw VGCF (2 wt %),
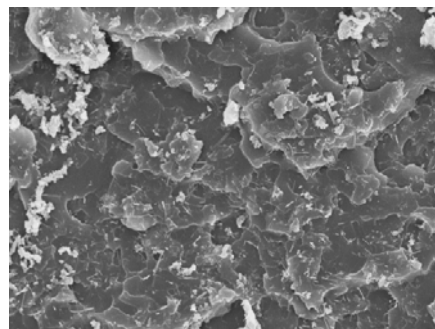mechanical mixing

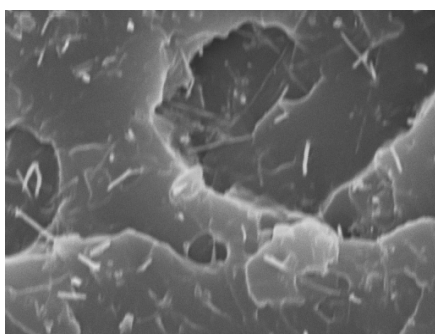Fig.15: raw VGCF (2 wt %),
homogenizer method

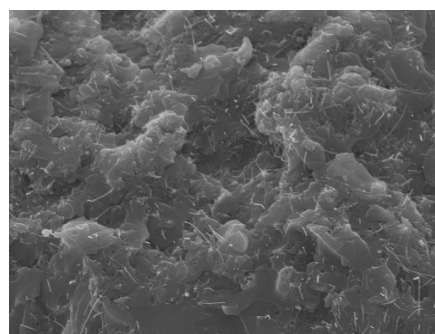Fig.16: raw VGCF (2 wt %),
ultrasonic method

Fig.17: APT VGCF (3 wt %),
ultrasonic method

SEM showed an excellent dispersion of raw VGCF and APT VGCF in epoxy matrix with solution blending and ultrasonic method (Fig. 15 ~ 17).

Using ethanol as dispersion solution, the raw VGCF and APT VGCF dispersed quite well in ethanol by applying ultrasonic and solution blending method for 30 minutes, respectively.

Conclusions

(1) The solution blending with alcohol, mechanical mixing, and ultra-sonication have been utilized to disperse VGCFs. Uniform distribution of fibers has been observed by SEM. The melt-mixed VGCF/PP rods of fiber volume content in the range of 4-31 % have been fabricated by twin-screw extrusion process. The rods were transferred into the mold, which was then subjected to compression by hot press.

(2) The addition of CNF into PP has resulted in reinforcing effect in the longitudinal direction. The tensile modulus and strength improved by 100% and 40%, respectively, for 31 % fiber volume content. For the same fiber content, the flexural modulus and strength have increased by 120% and 25%, respectively. The shear modulus showed 65% increase, but the strength dropped sharply by 40%. In the transverse direction, the tensile and flexural strength of composites decreased while moduli increase as more fibers are added. The addition of maleic anhydride (MAPP) increased the tensile and flexural properties of VGCF/PP by 20% - 30% in the longitudinal direction, and 40% - 250% increase in the transverse direction. The fiber surface treatment by plasma improved tensile and flexural properties of untreated VGCF/PP (18 % vol) composites by 10% - 30% in the longitudinal direction, but strength in the transverse direction decreased by 30% - 40%.

(3) With ethanol as a solution, the ultrasonic and solution blending method, respectively, provided well-dispersed raw VGCF and APT VGCF in the anhydride-cured epoxy matrix. However, tensile modulus and stregth of nanocomposites with solution blending method were lower than that of ultrasonic method. VGCF content 3.0 wt % provided highest modulus and strength.

(4) Atmospheric Plasma Treatment appears to have a positive effect in improving the interfacial bonding strength between VGCF and epoxy matrix. The tensile modulus of raw VGCF/epoxy matrix and APT VGCF/epoxy matrix were the same, but the tensile strength of APT/epoxy matrix were higher than that of raw VGCF/epoxy matrix with ultrasonic method.

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